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LIQUID PROPELLANT RESEARCH EVALUATION

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~~DOWNWARD SLOPE INTERVALS
DECLASSIFIED AFTER 12 YEARS
DOWNSIDE 5200.10~~

P. F. Winternitz / O. A. C.
Paul F. Winternitz
Project Director

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Abstract

Packageable and storable liquid propellants

Current liquid packageable propellant systems have a theoretical specific impulse of 270-290 sec.; theoretical density impulse is 440-470. For the 1970 era an I_{sp} of 300-350 sec. is projected.

Earth storable systems with an I_{sp} of 315 sec. and a vapor pressure not exceeding 500 psia at 165°F are being studied now; promising systems include slurries of Be, AlH_3 or BeH_2 in N_2H_4 or UDMH with N_2O_4 or mixtures of ClF_5 and N_2F_4 as the oxidizers.

8000 lbs. of Hybaline A5 have been delivered by Union Carbide. With N_2O_4 as the oxidizer an I_{sp} of 280 sec. (corrected to 1000 → 14.7 psia) was measured (89% of assumed theoretical I_{sp}). Performance exceeds that of the UDMH- N_2O_4 system by about 10 sec.

Thermal and storage stability of Hybaline A5 present problems.

Hybalines B, adducts of organic amines and $Be(BH_4)_2$, are probably more stable than Hybalines A. Their performance is better by a considerable margin. 10 lbs. of Hybaline B3 (adduct with methylamine) have been delivered so far. Firings in the open with solid grains containing beryllium have given according to preliminary evaluation unexpectedly low figures for air-contamination by beryllium. According to various experiments the combustion efficiency of both Hybaline A and Hybaline B should be promoted by the presence of CO_2 and water vapor in the combustion products. However, a high combustion temperature and an exhaust temperature below 900°C. is apparently required for efficient combustion of beryllium.

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With both BeH_2 and AlH_3 work is concentrating at present on product improvement. The average density of BeH_2 has been increased from 0.64 to 0.79. There are strong indications for a form of BeH_2 with a density of 1.1.

The BeH_2 obtained by metathetical reactions is at present always contaminated with 10-20% of impurities.

Chlorinepentafluoride, ClF_5 , a storable oxidizer will be available soon to industry. In compatibility, heat transfer etc. it resembles strongly ClF_3 . With various fuels it gives a theoretical I_{sp} higher by about 7% than CTF. But the increase in density impulse is considerably less. Rocketdyne obtained with N_2H_4 an experimental I_{sp} of 279 sec. at 300 psia chamber pressure corresponding to 96% efficiency. Correction to 1000 psia chamber gives an I_{sp} of about 300 sec.

OF_2 is probably the most energetic liquid oxidizer which can be synthesized. With N_2H_4 it gives a theoretical I_{sp} of 345 sec. and with B_2H_6 a theoretical I_{sp} of 367 sec. But the difficulties with the $\text{B}_2\text{H}_6\text{-F}_2\text{O}$ system have not yet been overcome.

Because of their sensitivity NF-compounds have not yet found practical application. Work concentrates, therefore, mainly on fundamental investigations including sensitivity studies.

Study of the reactions of perfluoroguanidine, a very important intermediate, has been extended to new classes of compounds such as perchlorates of amino alcohols, polyols and dinitramines. Amino alcohols have given interesting high energy salts (Info - xyz). Attempted desensitization of compounds "R" and "Δ" by dilution with N_2F_4 gave in the field disappointing results.

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A perchlorate containing the cation NH_3F^+ has been prepared by Aerojet.

Work on various mixed oxidizers is intended to improve properties and increase I_{sp} and ζI_{sp} of neat oxidizers. Constituents proposed include CTF, CPF, N_2F_4 , ClO_3F , compound "R", compound "A", etc. Certain improvements in properties have been obtained but in various instances explosions have occurred. Although work with mixed oxidizers is continuing field tests have apparently been postponed until an evaluation of safety aspects has been completed.

Cryogenic mixtures of liquid fluorine and liquid oxygen are studied as replacement for F_2O because of their higher versatility. Such mixtures are considered for use in the Atlas engine as a substitute for LOX.

Solutions or suspensions of various solid oxidizers in oxidizing liquids are also investigated. NO_2ClO_4 would be an excellent additive. RETA coating developed by Union Carbide gives the most effective protection for NO_2ClO_4 available at present. It will possibly permit the use of NO_2ClO_4 in solid propellants. For application to liquid propellants much further improvement will be necessary.

Gels and Slurries

Gelation of liquid rocket propellants has the purpose of increasing safety, raising performance and possibly also improving properties.

Particulate gellants together with surface agents and cross linked swellable gellants give satisfactory gels for many rocket propellants, particularly of the amine type fuels. Swellable gellants are preferable as a rule.

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Thixotropic gels with yield points between 300 and 1200 dynes/cm² are desirable as rocket propellants.

Hydrazine can because of its polarity be gelled only with swellable gellants. The gel (prepared with Carbopol) breaks easily down (high temperature, CO₂, etc.).

Slurries formed by suspending metal or metal hydrides give in theory increased performance; accurate experimental data are missing, but a combustion efficiency of at least 92% is necessary to make the conversion of the Titan 2 fuel to alumazine worth while.

Real improvement in performance is to be expected only from slurries containing AlH₃, Be or BeH₂.

It has been established that shock- and impact sensitivity of gelled propellants is much lower than that of the respective neat compounds. Improvement of other characteristics will be studied.

Uniform methods for preparation of gels and slurries, specification of properties, development of adequate test equipment and instrumentation and evaluation of gelled propellants in actual tests are needed for further progress.

Monopropellants

Investigations have been initiated to replace the heterogeneous systems B₄C slurried in IRFNA or N₂O₄ by other combinations because they are chemically not quite stable.

The liquid monopropellant Isobel F 2.6 is an off the shelf gas generant. Attempts to simplify hardware by using the gelled monopropellant

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encountered difficulties with ignition and combustion.

Otto fuel, composition 2, has reached pilot plant production and practical application. Large production is in preparation.

Propellant Systems

The space-storable system $F_2O-B_2H_6$ requires much further work before becoming operational.

B_5H_9 can substitute for UDMH in combination with IRFNA only in special applications.

Work on the $B_5H_9-N_2H_4$ system had to be discontinued because 90% efficiency was not consistently obtained and because of combustion instability at high performance.

The complexity of the system including its combustion is blamed for the failure.

In contrast to the B-N systems the LH_2-LOX system is uncomplicated. it gives high efficiencies even with very simplified injectors and engines. It is claimed that also other propellant systems can operate on simplified design. Combustion instability remains a problem with the LH_2-LOX system. Temperature effects (insufficient evaporation of LH_2) are not a satisfactory explanation for combustion instability. However, in practice proper design and baffling prevent combustion instability.

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I. Introduction

The present liquid propellant research evaluation covers the period from October 1st to December 31st, 1963. During this period the 5th Liquid Propulsion Symposium was held in Tampa, Florida, (Nov. 13th to 15th, 1963). The Interagency Chemical Rocket Propulsion Group sponsored the Symposium and the Army Material Command, Washington, D.C., acted as the host.

No detailed and coherent account of this meeting is given for a number of reasons. The meeting was attended by practically every organization interested in liquid rocket propellant, usually by more than one representative; some of the papers gave an evaluation of the past, present and future of liquid propellant research; summaries of all papers had been prepared and were distributed before the meeting and the complete text of all papers is now being printed and will be made available to all attendants in the near future.

This will, of course, not prevent us to use this meeting as a very important source whenever this will help in making a point or when it will supplement information collected in some other way.

Some of the sources used in the present report besides the TAMPA meeting are the following:

- 1.) A large number of progress, quarterly and final reports obtained from different contractors; (they are listed in the bibliography);
- 2.) Information collected from various organizations on the West Coast during a trip in December 1963, (the pertinent information has in many cases not yet been published);

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3.) Papers presented at the JANAF Thermochemical Panel meeting (New York, 5th - 7th November 1963) and at the AIAA "Heterogeneous Combustion Conference" (Palm Beach, December 11th-13th, 1963); *)

4.) Various telephone conversations and oral communications.

The present report follows in the whole the organization of the seventh quarterly research evaluation. Recent thermodynamic data have been included. Some of it is being reported when discussing particular propellants; other data is given in a brief summary of the JANAF Thermochemical Panel meeting.

The reader of this evaluation may end up with the feeling that during the report period progress has not been achieved in all areas. In fact he may think that in the future only small improvements can be expected because the theoretical limits of chemical propellants have been approached rather closely. A number of speakers at the 5th Liquid Propulsion Symposium expressed views along these lines. It can easily be seen that this is not quite correct. For instance, the specific impulse of current storable, liquid propellants is around 270-290 sec.; about 340-350 sec. should be obtainable with propellant combinations now being under investigation - an increase of nearly 20% !

This single example shows that a lot of propellant research and development will have to be done before all possibilities of chemical propellants have been exhausted. Of course, it cannot be expected that every three months a real break-through can be achieved - to use a much abused expression.

*) I am indebted to Dr. Phillip Pizzolato, The Martin Co., for making available to us notes taken at the AIAA meeting.

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II. Packageable and Storable Liquid Propellants

A. General Remarks

At the 5th Liquid Propulsion Symposium a number of speakers from the services as well as from private organizations reviewed present and future capabilities of rocket propulsion.

The theoretical specific impulse of current liquid packageable propellant systems was estimated by a representative of the Bureau of Naval Weapons to be in the range of 270-290 sec. The theoretical density impulse which is quite important in many applications varies from 440 to 470. (This is about 10% lower than the desired figure of 510 sec.).

An increase of the specific impulse to 300-350 sec. is projected for the 1970 era; (ref. 1).

A representative of the Air Force gave similar figures. They were in the whole the same as those given at the metallized gelled propellants conference and reported in Table III, p. 8 of the Sixth Liquid Propellant Research Evaluation (ref. 2).

Along the same lines ARPA and the Army have initiated a program towards the study of advanced high-energy, packageable liquid propellants. According to Aerojet General, the contractor, its objective is "the characterization and evaluation of liquid propellants which, in proper combination, yield earth-storable liquid propellant systems having a theoretical Isp of not less than 315 sec. Earth-storable systems are defined as those which are packageable, storable and semi-storable (storage pressure less than 500 psig at 160°F.)". (Ref. 3). The program includes theoretical performance calculations and experimental studies of selected systems. Besides the usual

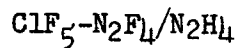
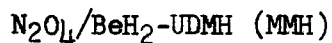
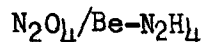
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physical-chemical data properties such as detonation propagation, materials compatibility and combustion characteristics (including c^*) will be determined. Also toxicology of new propellants will be reviewed and studied.

The first quarterly report contains an interesting review of theoretical performance calculations. It gives also tables for the properties of many recently developed propellants.

But it is not within the scope of this report to repeat here all the data presented. The interested reader must be referred to the original report. Aerojet states that the following systems are the more promising:



The theoretical performance figures for these systems and a few others are given in the following Table I which has been abstracted from various sections of reference (3):

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Table I.

Theoretical performance of high-energy, storable liquid
propellant systems

System	Mixture Ratio O/F	Isp(max.) Sec. 1000/14.7	Remark
$N_2O_4/AlH_3-N_2H_4$	0.56	318	48% b.w. AlH_3 in N_2H_4
$N_2O_4/Be-N_2H_4$	0.52	326	21% b.w. Be in N_2H_4
N_2O_4/BeH_2-UDMH	1.15	318	30% b.w. BeH_2 in UDMH (BeH_2 assumed 94% pure)
$ClF_5-N_2F_4/N_2H_4$	3.00	325	ClF_5/N_2F_4 : 33/67 b.w. ΔH_f of ClF_5 assumed -60 Kcal/ mole
N_2O_4/BeH_2-MMH	0.97	324	30% b.w. BeH_2 (94%) in MMH
	1.27	335	50% b.w. BeH_2 (94%) in MMH
$ClF_5/Be-N_2H_4$	2.85	317	25% b.w. Be in N_2H_4

A few remarks to this table and to the selection of propellant systems are pertinent.

1.) Numerous performance figures are given for systems incorporating compound "R", compound "T", PFG and mixed oxidizers. Among the selected systems none of these ingredients appears. Clearly they are not considered ready for application. (A mixture of ClF_5 and N_2F_4 is the exception).

2.) Also Hybaline A5 and Hybaline B3 are not among the selected propellants although they meet, with N_2O_4 as the oxidizer, the specifications of the

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program. Hybalines are discussed farther below in this report.

3.) Only packageable systems are taken into account. Storable and earth-storable systems are not considered. No performance figures are given for system incorporating hydrogen peroxide which gives with Be or BeH₂ higher performance than any other oxidizer.

4.) Density impulse is not reported. Systems containing Be or BeH₂ look much less attractive where density impulse is important.

5.) None of the selected systems is ready for immediate application. The first three contain metallized slurries and, with the possible exception of alumizine, data on such systems is quite limited. The fourth system involves a mixture of ClF₅ and N₂F₄. In view of experience with other mixed oxidizers this combination will have to be handled with extreme caution.

B. Liquid Fuels

1. Amine type fuels.

The general status of amine type fuels was discussed by Reaction Motors Division (ref. 4) at the Tampa Meeting. Research and development with this type of fuels has turned in the main to gels and slurries. In fact, most of the slurries considered for practical application have an amine-type base. Gels and slurries are discussed in section D of this report.

2. Hybalines *)

8000 lbs. of Hybaline A5 have been delivered by Union Carbide, namely about 3400 lbs. to Edwards AF Base, a little more than 3000 lbs. to Bell Aerosystem

*) In order to avoid repetitions the reader is also referred to reference 2, p. 4 ff. and reference 5, p. 4 ff. for information on Hybaline A5 and Hybaline B3.

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and various small amounts to different organizations (ref. 6); the active hydrogen content of the freshly prepared material varies according to Union Carbide from 92.6% to 97.4%. Hybaline A5 gave with N_2O_4 as the oxidizer at Edwards AF Base an Isp of 255-262 sec. at 500 psia chamber pressure and at a thrust level of 2000 lbs. (ref. 7 and 8); this figure corresponds to about 280 sec. for expansion from 1000 to 14.7 psia. The Isp efficiency is 89% of the assumed theoretical Isp of 315 sec. (The density impulse would be accordingly 353 sec.). But the uncertainty about the correct theoretical values of all Hybalines (ref. 5) has still not been resolved.

In any case, the experimental performance is about 10 sec. better than that of the propellant system UDMH- N_2O_4 . This is certainly a nice increase but "nothing spectacular" (reference 7). But it is sufficient to consider Hybaline A5 with IRFNA as the oxidizer as a substitute for UDMH. The cost of the Hybaline A5-IRFNA system is, however, about three times higher than that of the UDMH-IRFNA system.

Hybaline A5 presents also thermal and storage stability problems. It decomposes already at room temperature and develops within a short period of time considerable hydrogen pressures. Venting is necessary. This is a serious draw-back. According to Union Carbide the decomposition is slowed down by storage in Teflon and stopped by storage under hydrogen at 1000 psia.

The instability of Hybaline A5 is not quite unexpected; aluminum-hydride or aluminumalkyl adducts with amines or substituted amines release hydrogen or hydrocarbons if any hydrogen is attached to the nitrogen of the amine. Such is, of course, the case with the hybalines "A". Here primary or secondary amines are complexed with aluminumborohydride which because of its

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non-ionic character reacts frequently as $\text{AlH}_3(\text{BH}_3)_3$.

Possibly in an effort to reduce the hydrogen evolution of Hybaline A5 much attention is now given to Hybaline A4 which contains no primary amine. It will, of course, give a slightly lower Isp than Hybaline A5.

The properties of Hybaline A5 and Hybaline A4 are compared in the following Table 2.

Table 2.

Comparison of the Properties of Hybaline A5 and Hybaline A4

	A5	A4
Formula	53% b.w. $\text{CH}_3\text{NH}_2 \cdot \text{Al}(\text{BH}_4)_3$ 47% b.w. $(\text{CH}_3)_2\text{NH} \cdot \text{Al}(\text{BH}_4)_3$	$(\text{CH}_3)_2\text{NH} \cdot \text{Al}(\text{BH}_4)_3$
Molecular Weight	108.74	116.62
Density gm/ml at 20°C.	0.736	0.759
Vapor pressure (mm Hg, at 25°C)	3	2
Freezing Point °C.	-50.0	-12.0
Boiling Point °C.	263.0	200.0
Viscosity, centipoises 20°C.	6.78	0.92
Thermal Stability (beginning decomp.) °C	282	110
Shock Sensitivity Kg-cm	120	120
Air Sensitivity	oxidizes slowly without ignition	
Heat of formation Kcal/mole	+ 4.5	+ 4.2
Auto Ignition Temperature °C.	150	150

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The heats of formations of both Hybaline A5 and Hybaline A4 are based on a heat of formation of +17.7 Kcal/mole for $\text{Al}(\text{BH}_4)_3$ a figure which is probably quite optimistic (see ref. 5).

The theoretical Isp of the Hybaline A5/ N_2O_4 and Hybaline A4/ N_2O_4 systems varies of course with the assumed heat of formation of $\text{Al}(\text{BH}_4)_3$. The following table compares these figures.

Table 3.

Comparison of the performance of Hybaline A5 and Hybaline A4

assuming various heats of formation of $\text{Al}(\text{BH}_4)_3$

(N_2O_4 oxidizer; expansion 1000 \rightarrow 14.7 psia)

$\text{Al}(\text{BH}_4)_3$ ΔH_f Kcal/mole	Hybaline A5 Isp sec.	Hybaline A4 Isp sec.
+ 17.7	315 ⁽³⁾	(307)
+ 3.0	312 ⁽³⁾	-
- 50	(309)	298 ⁽¹⁾⁽²⁾
- 75	308 ⁽³⁾	-
- 100	(307)	291 ⁽¹⁾

Figures in parenthesis are inter(extra)polated.

- (1) Given by Mr. T. Dobbins (ARPA) at the JANAF Thermochemical meeting, New York, on November 7th, 1963.
- (2) A figure of 300 sec. for the second (fuel rich) peak of Hybaline A4 was given assuming $\Delta H_f = -50$ Kcal/mole for $\text{Al}(\text{BH}_4)_3$.
- (3) Taken from the 6th Quarterly Progress Report of Union Carbide Chem. Co., Contract AF 04(611)-8164, period 3/15 to 6/13/1963.

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The theoretical performance of Hybaline A4 is appreciably lower than that of Hybaline A5; the improvement over N_2H_4 or UDMH obtained with Hybaline A5 has been about cut in half. Based on the discussion of the instability of Hybalines "A" it might have looked tempting to use tertiary amines in the preparation of Hybalines A because they contain no hydrogen attached to nitrogen. Extrapolation of the results of Table 3 indicates that the resulting fuel would have with N_2O_4 an I_{sp} about that of N_2H_4 . Unless considerations other than I_{sp} and cost enter into the picture the new compound would, therefore, be useless.

Hybalines B, adducts of $Be(BH_4)_2$ and organic amines will give in all probability less trouble with instability than given by Hybalines A. The reason is, of course, that $Be(BH_4)_2$ has much more salt-like character than $Al(BH_4)_3$. Also the specific impulse of Hybalines B will exceed that of Hybalines A by a substantial margin. Its magnitude will clearly depend on many variables such as the heat of formation assumed for the borohydrides, the type of Hybaline and the nature of the oxidizer used. But in the average an increase of about 20 sec. can be safely anticipated for comparable systems. In ref. (3) a value of 317 sec. is given for the I_{sp} of the system Hybaline A5/ N_2O_4 and a value of 338 sec. for the I_{sp} of the system Hybaline B3/ N_2O_4 .

About 10 lbs. of Hybaline B3, the mono-adduct of methylamine and berylliumborohydride, have been delivered by Union Carbide to Edwards Air Force Base. The following Table 4 (reference 6) supplements and supersedes a short list of the properties of Hybaline B3 given previously (Table 1, ref. 2).

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Table 4.

Physical Properties of Hybaline B3

Formula	$\text{CH}_3\text{NH}_2 : \text{Be}(\text{BH}_4)_2$
Molecular Weight	69.78
Density gm/cc at 20°C	0.667
Vapor pressure mm Hg at 25.8°C.	1.5
Freezing Point, °C.	- 23 ⁽¹⁾
Heat of Combustion	23, 695 ± 60 ⁽²⁾
Thermal Stability, °C.	0.8% decomposed after 11 hours at 100°C. (3)
Viscosity cp, 20°C.	5.0
Heat of Formation, Kcal/mole	- 11.0 ⁽⁴⁾
Flash Point, °F.	68.0
Auto Ignition Temperature °F.	284.0
Boiling Point °C.	270.0
Critical Temperature °C.	500
Air Sensitivity	Oxidizes slowly in air without ignition
Shock Sensitivity	120.0 ⁽⁵⁾

(1) true freezing point between -23 and -80°C.

(2) preliminary; not used in ΔH_f calculation.

(3) preliminary.

(4) estimate; ΔH_f of $\text{Be}(\text{BH}_4)_2$ assumed 0; NBS value taken for the amine ligand; estimated strength of coordination bond -5.0 Kcal/mole. Values up to -46 kcal/mole are quoted.

(5) limit of detection by LPIA test method.

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No performance figures have been published as yet for Hybaline B3. Its cost will certainly be quite high. But at the present level of production any quotation would be meaningless.

Another problem with Hybaline B3 is, of course, toxicity, a problem common to all beryllium containing propellants. Still, health hazards in open air firings may be less serious than anticipated. A preliminary evaluation of such firings by the AF (project Sandstorm) showed rather low concentrations of BeO in the surrounding atmosphere. M.I.T. is thoroughly evaluating the data at this writing.

The combustion efficiency of both Hybalines A and Hybalines B is interesting from a number of viewpoints. It might be expected to be determined by the combustion of the respective borohydrides. Now $\text{Al}(\text{BH}_4)_3$ does not only ignite spontaneously in air. It ignites and burns also in supersonic jets better than any other known material. Accordingly the combustion efficiency of Hybaline A should be quite high. On the other hand a much lower efficiency would result if the observations of many researchers on the combustion of aluminum and other metals are applicable (compare e.g. ref. 10) or if the claim is justified that dissociation of hydrides reduces combustion efficiency. The reported figure of 89% is certainly not unusually high; but it might be based on wrong theoretical values. An analysis of the exhaust products of Hybaline A firings might be helpful in clarifying this question.

Mellor and Glassman (ref. 14) have found that carbondioxide will substantially reduce the power required to ignite aluminum. A study of the effect of water vapor on the combustion of aluminum is planned. Both

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carbondioxide and water vapor are, of course, always present in the combustion products of Hybalines.

In this connection it might be of interest that water-vapor appears to substantially affect the combustion of beryllium. Be has long been known to burn satisfactorily only at very high temperatures and at elevated pressures. But now it is claimed that for satisfactory efficiency also the expansion ratio must be high enough to reduce the exhaust temperature to at least 900°C. because BeO supposedly forms at elevated temperatures a stable gaseous hydroxide which decomposes under release of heat only at that temperature. A number of papers are quoted in support of this assumption (ref. 11 and 13). An increased volatility of BeO in the presence of water vapor is also reported in a recent paper by Rocket Power (ref. 12). But high-melting oxides inhibit combustion, which should, therefore, be promoted by increasing volatility.

The presence of boron in the hybaline molecule should equally improve combustion efficiency; boron has a very high heat of combustion and the presence of boronoxides will certainly depress the melting point of aluminum- or beryllium oxides. Both factors will contribute to the destruction of a solid oxide shell.

Clearly some of the thoughts outlined above can be applied also to the combustion of liquids or slurries containing Be and Al or their hydrides. But the scope of the present report does not permit to enter further into this subject.

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3.) Light Metal Hydrides .

Because of their planned application in liquid rocket propellants the hydrides of beryllium and aluminum have been discussed in some detail in references (2) and (5). During the present report period work in this area proceeded steadily in the direction indicated in these reviews; no startling new development can be reported. Rather it was a period of consolidation. The Dow Chemical Co. puts it this way: "Synthesis routes for both hydrides are well established and the work is concentrating on product improvement." (ref. 15).*)

Dow Chemical is investigating the details of the production process. They describe also the installation and starting up of a new improved processing plant for the production of macrocrystalline AlH_3 -1451. During the quarter 1650 gms of propellant grade AlH_3 were made in the mini-plant. It will be attempted to replace the LiBH_4 used presently in the process by NaBH_4 .

Also Olin Mathieson is making a detailed study of the reaction conditions and their effect on the yield and properties of AlH_3 . (ref. 17).

Both manufacturers and many of their customers continue to investigate the stability of AlH_3 . Results obtained depend on many factors, such as experimental conditions, source of the material, crystal form and size, etc. It makes for instance, quite a difference whether stability is

*) Remark: We agree in general with this statement as far as present work is concerned; but we take exception to the claim that "synthesis routes are well established"; they are not. Better synthesis routes are urgently needed for both hydrides.

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observed in nitrogen, air or argon, whether the material is tested under vacuum and whether it has been "stabilized" or not. It is, therefore, somewhat difficult to compare results for the materials obtained from the two companies. But on the whole the "propellant grade" material delivered by both Olin-Mathieson Chemical Corp. and Dow Chemical Co. is thermally stable at 60°C. After four days at this temperature depending on the conditions about 0.1% to 0.2% of AlH_3 -1451 (also called Dowane 1451) decomposed, whereas 0.094% decomposition is reported for Olane 58. At 85°C. decomposition is already much faster - after 24 hours 75% of AlH_3 -1451 had decomposed. A substantial difference is reported in the heats of formation for the AlH_3 from these two sources. The variance is much higher than can be explained by differences in the purity of the samples.

Values reported at the JANAF Thermochemical Panel meeting in New York, in November 1963, are compared in the following table (ref. 16).

Table 5.

Comparison of heat of formation reported for AlH_3

(Kg cal/gm mole)

Source	AlH_3 (no description)	AlH_3 -1451 94.3 - 94.7%	Olane 58 97.2%
NBS	- 3.0	-	
Dow	-	- 2.76 \pm 0.15 ⁽¹⁾	
Olin	-	- 2.9 \pm 0.6	- 4.7 \pm 0.7
National Research	-	- 2.5 \pm 3.7	- 4.6 \pm 1.6

(1) average value

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A difference in thermal stability corresponding to the difference in the heat of formation would be expected; but the data on stability are not accurate enough to be correlated to the thermochemical data.

Reports on the preparation of liquid AlH_3 have not been confirmed.

The production of BeH_2 is considerably greater than that of AlH_3 but otherwise the situation is very similar to that with AlH_3 .

The process used by Ethyl Corporation is still solution pyrolysis of t-butyl beryllium etherate. The purity of the material, called BEANE, has not been improved. Ethyl Corporation claims a purity of 95-96%, but some customers have received occasionally material having a purity as low as 93%. This figure is further reduced to well below 90% if the material has to be finely ground, (slurries, combustion in solids) even if grinding is done in an inert atmosphere (ref. 8). The average density is now 0.79, a substantial improvement over the older figure of about 0.64. The higher density is apparently obtained by the pressure and heat-treatment described in reference 5, which converts the amorphous material obtained by solution pyrolysis to a largely crystalline material. The metathetical reaction being investigated by Ethyl Corporation (ref. 5) gives without treatment already a product with a crystallinity of about 60%. Ethyl Corporation has also "strong indications" that the metathetical product contains about 20% BeH_2 with a density of 1.1. Unfortunately the metathetical reaction gives so far only a product containing about 20% of impurities. Also Dow Chemical could not reduce the amount impurity in the product obtained from the metathetical reaction of LiAlH_4 and $\text{Be}(\text{BH}_4)_2$ (ref. 15) below the figure of 10% AlH_3 .

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Many attempts to prepare BeH_2 by other routes have been summarized in Table VI of reference (5).

A new approach is reported by Rocketdyne (ref. 18). In an effort to synthesize new liquid beryllium compounds for use as rocket propellants they attempted to eliminate BH_3 from the known dimer of BeCH_3BH_4 ; they expected a liquid with the formula CH_3BeH . However, CH_3 was released simultaneously with BH_3 and the solid end product contained 77% of BeH_2 . It seems that the purity could not be increased further. The performance of BeH_2 with various oxidizers is quite high. This is shown in the following table taken from reference 19.

Two series of figures are given assuming two different values for the heat of formation of BeH_2 ; the value reported by NBS (ref. 16) and confirmed by Dow Chemical Co. is -4.5 Kcal/mole for a sample of 95-96% purity.

Table 6.

Performance of BeH_2 with various Oxidizers

Oxidizer	Isp(sec.) 1000 → 14.7 psia	
	$\Delta H_f = 0$ Kcal/mole	$\Delta H_f = -5.6$ Kcal/mole
F_2	376	370
OF_2	361	355
O_2	356	350
N_2F_4	347	341
H_2O_2	363	357
N_2O_4	336	330
ClF_3	315	310

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In a hybrid propellant system the BeH_2 has to be incorporated in some binder; 20% polybutadiene will reduce for instance the performance with H_2O_2 as the oxidizer from 357 sec. (2nd column) to 350 sec. Also for liquid propellant applications of BeH_2 a carrier is required. If H_2O_2 is used as such there is no reduction in performance at all. For the I_{sp} of the system $\text{H}_2\text{O}_2\text{-BeH}_2/\text{N}_2\text{H}_4$ even a figure of 370 sec. has been quoted (ref. 4).

Efforts to improve existing processes for the manufacture of BeH_2 are certainly justified by this high performance. Unfortunately these efforts have been unsuccessful so far. But enough leads have been obtained to take an optimistic view of future developments.

C. Liquid Oxidizers

1. Interhalogen Compounds

Chlorinepentafluoride, ClF_5 , code-name compound "A", is being produced by Allied Chemical Co., Morristown, N.J., on a pilot plant scale (ref. 5). The demand by the services seems to exceed present production capacity, but the material will be available to industry very soon "in the foreseeable future" (ref. 20). In the meantime, many organizations are preparing research quantities on a small scale. Lacking pressure equipment the best laboratory method is apparently reaction of CsClF_4 with chlorine-trifluoride (ref. 21). Rocketdyne claims that compound "A" can also be obtained by dissolving ClF_3 in anh. HF and bubbling Cl_2 through the solution. Salts containing the ClF_4^- anion can be prepared in this way. ClF_5 is also produced in trace amounts by electrolyzing the system HF-NaF-Cl_2 (ref. 22).

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A revised summary of the properties of compound "A" is presented in Table 7, which has been abstracted from a CPIA publication (ref. 23)

Table 7.

Properties of Chlorine Pentafluoride

(CPF or compound "A")

Formula	ClF ₅
Molecular Weight	130.5
Boiling Point	-114°C.
Melting Point	-103 ± 4°C.
Liquid Density (range -78 to -20°C.)	2.61 - 0.0029T°K.
Liquid Density at 25°C.	1.74 gm/cc
Critical Temperature (calc.)	117°C.
Critical Pressure (calc.)	43 atm.
Critical Density (calc.)	0.713 gm/cc
Heat of Vaporization	5.33 Kcal/mole
Heat of Formation (vapor)	-52.7 ± 2 Kcal/mole
Trouton Constant	22.5
Chemical Properties	quite similar to CTF slightly more reactive with H ₂ O ⁽¹⁾
Materials Compatibility	very similar to CTF
Drop Weight Test	negative to 600 in-lbs.
Detonation Propagation	negative
Toxicity	about the same as CTF

Requests for samples (up to 1 lb.) to be directed to Dr. John Crowder, Allied Chemical Corp., Morristown, N.J. (copies to ARPA and AMC, Huntsville, Att. Dr. W. Wharton)

- (1) The principal product of reaction with water is chloryl fluoride, FClO₂, with some FClO₃ and ClO₂ also being formed (ref. 27).

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Picatinny Arsenal (LRPL) studied recently long time storage of CTF in various materials of construction (ref. 24). According to the statement in Table 7 it can be anticipated that also compound "A" is compatible with aluminum alloys, stainless steel, nickel, inconel, titanium and tantalum. But only Teflon should be used as a material for O-rings and similar applications. Also the heat transfer of ClF_5 and ClF_3 are practically equal. Compound "A" is compatible and miscible with many high-energy oxidizers such as $\text{C}(\text{NO}_2)_4$, CTF, F_3NO , N_2F_4 , ClO_3F , Moxy 2a; it is, therefore a promising constituent of mixed oxidizers.

The Army Missile Command, Redstone Arsenal, compared the physical properties of three halogen-based oxidizers in the following table (ref. 25):

Table 8.

Physical Properties of three halogen based oxidizers

	ClF_3	ClF_5	ClO_3F
M.P. °C.	-82.6	-103	-146
B.P. °C.	11.3	- 14	46.8
ΔH_f^{25} K-cal/mole	-44.4	- 58 ⁽¹⁾	-10.1
d^{25} g/ccm	1.81	1.75	1.43

(1) liquid

The heat of formation of ClF_5 has been corrected to agree with the recent figure listed in Table 7 above. According to T. Dobbins, ARPA (ref. 16) a slightly higher value of -59 to -60 Kcal/mole is probably correct. Even so ClF_5 has potentialities as an oxidizer for storable liquid propellants. Its specific impulse is in the average about 7% higher than that of CTF;

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however, the increase in density impulse is far less because of the effect of mixture ratio. (The percentage by weight of CPF required is smaller because, having about the same density, it contains more fluorine !)

Compound "A" is also less energetic than N_2F_4 . A few figures for compound "A" are given in the following table collected from various sources.

Table 8.A

Theoretical Performance of Compound "A" in various Propellant Systems

(1000 \rightarrow 14.7 psia)

Oxidizer	Fuel	Isp sec.	ξ Isp
ClF_5 (100%)	N_2H_4	312	451
ClF_3 (100%)	N_2H_4	294	444
ClF_5 80%/ N_2F_4 20%	N_2H_4	315	-
N_2F_4 (100%)	N_2H_4	332	-
ClF_5	B_2H_6	316	-
ClF_5	B_5H_9	308	426
ClF_5	N_2H_4 - Al	302	492
ClF_5	N_2H_4 - Be	329	-

Rocketdyne has obtained 96% efficiency with the propellant system ClF_5/N_2H_4 using a 500 lb. thrust motor and operating at a chamber pressure of 300 psia. They measured an Isp of 279 sec. (compared to 260 sec. delivered by the ClF_3/N_2H_4 system). With various configurations of chamber and injector the difference between the CTF and CPF systems was consistently in the range from 17 to 19 sec.; the Isp efficiency of the ClF_5/N_2H_4 system varied from 94-98% (ref. 26).

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Compound "A" will be used in the 2nd and 3rd generation of missiles to push a high payload out of the "hole" (the term used universally for the storage silo). It appears that its first application will be in Navy missiles because this branch of the services places the greatest emphasis on prepackaging. CTF having been accepted for shipboard use, the Navy will obviously also not object to the use of ClF_5 .

The Air Force is requesting bids for the production of about 1-1/2 tons of compound "A". Pennsalt (North American), Harshaw Chemical, and Allied Chemical are competing. Rocketdyne shipped small amounts of "fluoridyne" (compound "A") to NOTS and R & D.

2. Oxygendifluoride, OF_2

Oxygendifluoride can be obtained from General Chemical Div., Allied Chemical, either as a liquid in refrigerated transport tanks or as a compressed gas at 400 psi pressure.

It is probably the ultimate in space storable liquid oxidizers (ref. 29). Therefore, work towards its practical application is being intensively pursued at the present time (after an interval of about 10 years). But the position of F_2O is not quite unchallenged. It has still to compete with other oxidizers used specifically with physical mixtures of fluorine and oxygen (called FLOX).

Because of the high performance of F_2O it may be of some interest to summarize a few figures which were reported in reference 28 a few months ago.

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Table 9.

Performance of F₂O with some Fuels

(1000 → 14.7 psi)

	<u>I_{sp} (sec.)</u>	<u>g I_{sp}</u>
H ₂	411	158
B ₂ H ₆	367	300
Aerozine	351	439
N ₂ H ₄	345	438
RP1	350	469
Hybaline B3	367	415
B ₅ H ₉	359	-

It might be of interest to list the performance of some hypothetical oxidizers containing oxygen and halogen and to compare the figures with those given in Table 9 (or the last line in Table 10).

Table 10.

Performance of some hypothetical High Energy

Oxidizers with B₅H₉ and N₂H₄

(1000 → 14.7 psia)

	<u>B₅H₉</u>	<u>N₂H₄</u>
ON(OF) ₃	355	-
F ₂ NOONF ₂	342	329
ONF ₃	325	-
OC1F ₅	-	320
OF ₂	359	345

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The I_{sp} of OF_2 exceeds all of these hypothetical oxidizers not a single one of which has been prepared so far (ref. 29).

F_2O has also a very high combustion efficiency (RMD reported 100% c^* efficiency; ref. 2) but unfortunately it seems that some of the difficulties connected with its use have not yet been overcome. One hears occasionally that OF_2 is worse than fluorine, and that it looks less good than a year ago. This may be an isolated opinion, but certainly a lot of work remains to be done before the $F_2O-B_2H_6$ system has been reduced to practice. Among the data urgently needed for the design of reliable engines are the heat transfer properties of F_2O . Because of the existing uncertainty regarding these properties they have not been included in the following table which summarizes some of the properties of F_2O .

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Table 11.

Some Properties of Oxygendifluoride

Formula	OF ₂
Molecular Weight	54.00
Melting Point	-223.8°C.
Boiling Point	-145 °C.
Critical Temperature	-58.0°C.
Critical Pressure	48.9 atm.
Critical Density	0.553 g/cc
Vapor Pressure log P _{mm} Hg	$7.2242 - \frac{535.42}{T^{\circ}\text{K}}$
Density of Liquid	
at Boiling Point	1.521 g/cc
as function of temperature	$2.190 - 0.00523 T^{\circ}$ (-153 to -145°C.)
Heat of Formation (at 0°C.)	7.6 ± 2.0 Kcal/mole
Heat of Vaporization (at Boiling Point)	2.680 Kcal/mole

(Reference: Product Data Sheet on Oxygen Difluoride, General
Chemical Division, Allied Chemical Corp., New
York, N.Y.)

Some of the figures of this data sheet might have to undergo
revision; specifically the heat of formation of gaseous OF₂ has
been found by Rocketdyne to be -3.2 ± 0.3 Kcal/mole (ref. 16;
compare also ref. 5).

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The compatibility of OF_2 with various materials of construction was briefly discussed in reference 5. Reaction Motors is preparing under AF-contract a detailed report on the properties of OF_2 . The table in Appendix A was kindly made available to us prior to publication; it gives a detailed survey of materials of construction which can be used with OF_2 for various purposes.

Various organizations are studying reactions of OF_2 with organic and inorganic compounds. General Chemical Div. reported the preparation of the compound FSO_2OOF from $\text{FSO}_2\text{OOSO}_2\text{F}$ and OF_2 (ref. 30). Although the new compound as such holds, of course, no promise as a rocket propellant introduction of the "peroxy-OF" group into other molecules might give interesting results.

3. N-F Compounds .

A considerable portion of the effort in fluorine chemistry is still devoted to N-F compounds; but synthetic efforts appear to be leveling off in favor of a closer look at existing compounds.

The high sensitivity of practically all NF-compounds is still a very serious problem. In solid propellants NF-compounds are to be used at least at present, primarily as binders and plasticizers. Although sensitivity might be overcome in these applications, frequently the mechanical properties of NF-polymers cannot meet specifications. In liquid propellant systems NF-compounds are to be used as high-energy oxidizers. It was attempted to reduce for these applications sensitivity of compounds such as $\text{CF}(\text{NF}_2)_3$ and $\text{C}(\text{NF}_2)_4$ by adding inert materials e.g. N_2F_4 , CTF, etc. Laboratory experiments looked promising. But engine tests were disappointing.

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These are the main reasons why in the areas of both solid and liquid rocket propellants the greatest portion of all work has still to be devoted to fundamental studies.

In the field of liquid propellants these fundamental studies are concentrating on the sensitivity problem and on basic chemistry. In this situation it is quite uncertain which one among the new compounds, if any, will be used as a constituent of liquid rocket propellants or as an intermediate to such constituents. It does not appear profitable to discuss again in detail all compounds which have been prepared. Rather we will limit ourselves to a brief evaluation of developments which hold some promise. A review of the status of NF-chemistry has anyway been given a short while ago (ref. 5).

The most important intermediate in the synthesis of NF-compounds with a high NF_2/C ratio is undoubtedly perfluoroguanidine, PFG. Its structural formula is $\text{NF}=\text{C}(\text{NF}_2)_2$. Its properties have been listed before, (ref. 2, p. 20). Also the processes used by American Cyanamid and Callery Chemical Co., the main sources of PFG, have been discussed. MMM has improved the direct fluorination of ammeline to a point where in a 1500 ml reactor PFG or compound "R" are the major product according to the chosen conditions (ref. 31). But apparently there is still a shortage and DuPont is building its own facility (aqueous fluorination of guanidinium fluoride) capable of producing 100 gm/run.

The reactions of PFG with alcohols, amines and isocyanates leading to products containing the $-\text{C}(\text{NF}_2)_3$ group are well known. More recently attention is given to its reactions with the perchlorates of amino alcohols, polyols and dinitramines. Of particular interest are the reactions of PFG

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with the perchlorates of amino alcohols. Fluorination of the salts formed in this way gives compounds which are apparently more energetic oxidizers than nitronium- or ammoniumperchlorate. Provided the sensitivity problem can be solved solutions or slurries of these materials might give useful oxidizers for liquid propellant systems.

The adduct of $\text{OH.NH}_2.\text{HClO}_4$ and PFG gives on fluorination supposedly the attractive salt $(\text{F}_2\text{N})_2\text{C}(\text{NF}_2).\text{ONH}_2.\text{HClO}_4$. But the reaction does not proceed smoothly (ref. 31, 32). The analogous product derived from ethanolamine gives in the laboratory in 47% yield the ionic salt $(\text{F}_2\text{N})_3\text{C-O-CH}_2.\text{CH}_2\text{NH}_2.\text{HClO}_4$, called INFO-635. It is not hygroscopic, melts at $195-196^\circ\text{C}$. and has an impact sensitivity of 6 kg-cm. Scaling up is attempted by both DuPont and MMM. Salts with an even higher energy content than INFO-635 are being studied now.

Nitroalcohols give with PFG compounds containing NF_2 and NO_2 groups in the same molecule. This type of compounds is discussed in section 4.

The heat of formation of F_{11}BG , the completely fluorinated biguanide, is so high that it cannot be considered to be a useful oxidizer. F_7BG is still of interest as starting material for high-energy polymers (ref. 5) but its synthesis is quite ineffective (2% yield).

Direct fluorination of azodiformamidine dinitrate has given the perfluoro derivative with the formula $(\text{NF}_2)_2\text{CFN=NCF}(\text{NF}_2)_2$, code F_{10}ADF . It is a liquid, boiling at 82°C and does not react at room temperature with NaOH or HCl . Reduction followed by fluorination may possibly convert F_{10}ADF into compound "R", $\text{FC}(\text{NF}_2)_3$.

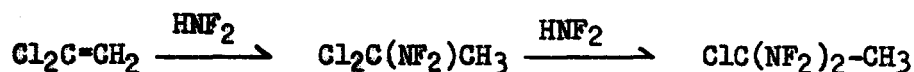
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Another roundabout way to prepare compound "R" was discovered by MMM; (ref. 31) it consists of the reaction of $\text{CF}_2(\text{OF})_2$ with PFG in the presence of KCN. This synthesis is obviously only of theoretical interest.

Compounds containing the group $-\text{C}(\text{NF}_2)_3$ can be considered as derivatives of compound "R". New methods to prepare such compounds are investigated.

Aerojet (ref. 33) did not succeed in converting the tricarbamate $\text{HC}(\text{NHCOOEt})_3$ by direct fluorination into compound "R". But they were able to add HNF_2 to 1,1-dichloroethylene and to replace one of the chlorine atoms of the addition product by NF_2 as shown in the equation:



Both compound "R" and compound "Δ", tetrakis (difluoroamino) methane, $\text{C}(\text{NF}_2)_4$ are very expensive compounds, compound "Δ" being the more costly one by far. The overall yield in its synthesis (ref. 2) is only about 1% and its cost is no less than \$10,000 per gm! (ref. 17). Clearly a better method for its preparation must be found before it can be considered as a propellant, even if it is assumed that the price of \$10,000/gm includes research and development cost.

It has been reported in reference 2 that diluting compound "R" and compound "Δ" with perfluorohydrazine reduces sensitivity by a factor of ten. Specifically a 1:1 mixture of compound "R" has been used in a mixed oxidizer called Mox 2a. (See below section on mixed oxidizers). From recent experience it must be concluded that results of laboratory tests are in this case not applicable to operations on a larger scale. In fact, one is tempted to say that unfavorable results of laboratory experiments indicate definitely that the particular propellant is dangerous. But a favorable result gives

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by no means assurance that it can be safely used in the field.

Both Ethyl Corporation and Callery Chemical Co. are discontinuing efforts to prepare metal derivatives of NF_3 or HNF_2 . According to the Ethyl Corporation the NF_2^- salts of Na or Cs are very unstable even at $-100^\circ\text{C}.$, if they exist at all (ref. 34). Work with heavy metals, although possibly successful, would not lead to useful oxidizers. Callery dropped work with boron and aluminum the only likely candidates to form MNF_2 salts because their strong tendency to form metal-fluorine bonds prevents the existence of useful M-N-F compounds (ref. 35).

The addition of N_2F_4 to double bonds is investigated further by a number of organizations. The reaction is used mostly for the preparation of NF-containing polymers, although the PFG-route is at present frequently preferred. But addition to cycloolefins e.g. tropilidene (cycloheptatriene) or 1,5 and 1,3-cyclooctadiene gave mostly high density liquid products. Again their high shock sensitivity prevents applications.

Among the many studies of a fundamental nature the search for ionic species such as NH_3F^+ , NHF_2^+ , NHF_3^+ and NF_4^+ and for their salts with the anions F^- , NO_3^- and ClO_4^- is of particular interest. Such compounds would be expected to be in general salt-like and hence solids. But depending on the degree of covalent character of the cation some of them might be liquids. Needless to say, a compound with the formula $\text{NH}_3\text{F}^+\text{ClO}_4^-$ would be an excellent oxidizer. Aerojet has definitely prepared this compound (ref. 33). They decarboxylated the carbamate NHFCOOEt in 70% HClO_4 and obtained a product contaminated with H_2O and HClO_4 . After some experimentation they succeeded in obtaining a pure product. They removed the H_2O and HClO_4 with dioxane, extracted the dioxane with ether and removed finally the ether by pumping.

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The existence of the NH_3F^+ ion had been demonstrated already before by Rohm and Haas (ref. 36). They had observed that the methanol adduct of PFG reacts rapidly with sulfuric acid under release of HNF_2 and CO_2 . NMR studies of the remaining H_2SO_4 solution indicated the existence of the NH_3F^+ ion.

Stanford Research Institute will look for ions such as OF^+ , NF^+ and NF_2^+ in anhydrous hydrofluoric acid. They will also attempt to obtain the NF_4^+ species by reacting an NF_3^+ ion beam with an F_2 molecular beam.

All these studies can, of course, bear fruits only in the more distant future. They are all leading up to the ultimate goal in oxidizer chemistry, namely the preparation of compounds containing the atoms N, O and F_2 in some combination which is only slightly less energetic than F_2O or F_2 while having superior physical-chemical properties.

As emphasized repeatedly sensitivity is possibly the most serious problem with NF-oxidizers. There is as yet no answer to the question why some NF-compounds are more shock-sensitive than other species of comparable inherent energy which do not contain NF-groups, nor are the reasons understood for the variations in the sensitivity of different NF-compounds. A number of organizations are trying to answer these questions.

As reported before Stanford Research Institute has found that 2,2-bis(NF_2)propane (2,2-DP) is much less shock sensitive than its isomer 1,2-bis(NF_2)propane (1,2-DP). The former is also chemically much more stable. It is claimed that splitting out HF is the primary step in the decomposition. Loss of HF was in fact the rate controlling step in the decomposition of the 1,2 isomer, whereas the decomposition of the 2,2 isomer was autocatalytic.

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Elimination of HF can, of course, not be the reason for the sensitivity of perfluoro-NF₂ or per-NF₂ compounds.

Other investigators claim that with compounds such as PFG and fluorinated biguanide small amounts of impurities are responsible for the high sensitivity. ICI found in PFG a high boiling very unstable compound believed to be perfluoroaminoguanidine (ref. 31). But Esso reports that even very careful purification did not improve the stability of a sensitive compound with the formula $[(F_2N)_3NHCONH]_2$ (ref. 32). They concluded that the instability was inherent to the compound. It seems that the high sensitivity of NF-compounds can as a rule not be blamed on impurities, although occasionally certain specific contaminations might be responsible. It is tempting to generalize the findings of SRI and to assume that the first step in the decomposition of NF-compounds consists in the elimination of stable compounds. HF would be only one of them; others might be e.g. F₂ or NF₃. It would still remain an open question whether this elimination would be as such the highly reactive process or whether it would only lead to a very unstable intermediate.

The elimination of HF, NF₃ or F₂ from molecules such as 1,2-bis(NF₂)-propane, 2,2-bis(NF₂) propane, compound "R" or compound "Δ" will give molecules which contain at the same time the difluoroamino and the fluoroimino group. The high sensitivity of PFG proves the instability of such structures. Also fluoroimino compounds have been found to be intermediates by S.R.I.

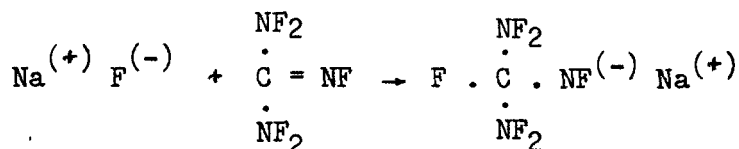
In this connection the role of NaF in the decomposition of the bis (NF₂) propanes is quite interesting. One would assume offhand that the decomposition rate would be accelerated by the presence of NaF because

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this salt absorbs HF. SRI found that the opposite is the case.

Now, NaF cannot react or form an adduct with either 1,2 or 2,2-bis (NF₂)-propane. But it is believed to react with the fluoroimino group e.g.



to form molecules with ionic character. If the reactive or autocatalytic intermediate in the decomposition of bis (NF₂) propanes is actually a fluoroimino compound and if the ionic molecule is actually formed the retarding action of NaF would, therefore, have to be expected.

Another explanation is, of course, also possible: if HF promotes the decomposition then its removal by NaF would clearly have a retarding effect. Addition of HF in the absence of NaF would decide between the two possibilities.

We would like, however, to conclude this discussion with the following remarks:

Because of the high electronegativity of the fluorine atoms the NF₂-group tends to withdraw electrons from the molecule; this weakens the C-C and C-H bonds in the vicinity of this group. It accentuates also the mobility of the hydrogen atoms attached to primary, secondary and tertiary carbon atoms although it does not change the order of their reactivity. The inductive effect of the NF₂-group decreases, of course, with distance. Therefore, the hydrogen atoms on the 1,2-DP are more labile than those in 2,2-DP which are remote by more than the length of one C-C bond from the carbon atom carrying the two NF₂-groups. Also the lability of the H atom

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attached to the carbon should increase as one proceeds from CH_3NF_2 to $\text{CH}(\text{NF}_2)_3$ in analogous manner as it does when proceeding from CH_3NO_2 to $\text{HC}(\text{NO}_2)_3$. Replenishment of electrons in the molecule should again normalize the situation. Accordingly the molecule $\text{H}_2\text{C}=\text{CH}-\text{NF}_2$ should lose HF with greater difficulty than the molecule $\text{CH}_3-\text{CH}_2-\text{NF}_2$.

Doubtlessly experiments will show that the discussion given above is oversimplified. But it may contain a grain of salt and be helpful in programming new investigations.

4. Compounds containing both NF_2 and NO_2 groups.

The advantages of such compounds as well as some prior work have been discussed in reference 2.

We can, therefore, limit ourselves to a brief review of recent progress.

Condensation of nitroalcohols and PFG, an excellent method for the preparation of such compounds, is being used by Esso for the synthesis of the salt $(\text{F}_2\text{N})_3\text{C}-\text{O}-\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_3^+\text{C}(\text{NO}_2)_3^-$ (ref. 32).

Stanford Research Institute continued previous work (ref. 38) and prepared various liquid compounds containing both NO_2 and NF_2 groups by reacting HNF_2 with organic substrates containing NO_2 -groups. The following table lists some of these compounds together with a few characteristics.

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Table 12.

Some Properties of Organic Compounds containing both -NO₂
and -NF₂ groups

<u>Formula</u>	<u>Appearance</u>	<u>B.P. °C.</u>	<u>Density</u>	<u>n_D</u>
(F ₂ N) ₂ CHCH ₂ CH ₂ C(NO ₂) ₃	clear, colorless liquid	65-70 (0.03 mm)	1.64(23°C.)	1.4358(22°C)
(F ₂ N) ₂ CHCH ₂ .CH(CH ₃)C(NO ₂) ₃	clear, colorless liquid	80 (0.03 mm)	1.57(22°C.)	1.4375(23°C)
(O ₂ N) ₃ CCH ₂ CH ₂ C(NF ₂) ₂ (CH ₂) ₂ C(NO ₂) ₃	clear, crystalline solid	73 (M.P.)	-	-
F ₂ NCH ₂ CH ₂ C(NO ₂) ₃	clear, colorless liquid	40-45 (0.25 mm)	1.59(26°C.)	1.4370(25°C)

Esso obtained the monoadduct of ethylenedinitramine (EDNA) and PFG which contains both -NF₂ and -N.NO₂ entities, but was unable so far to get a pure product (ref. 32).

5. N-NF₂ and N-NO₂ compounds.

The last compound mentioned in the previous section could also be classified as a nitramine, a compound containing the -N-NO₂ grouping.

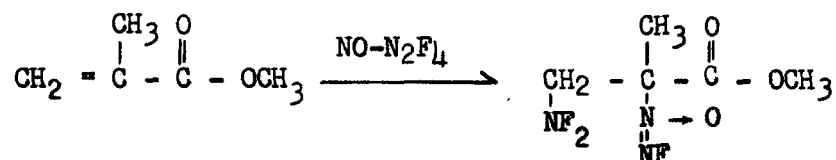
Nitramine compounds are, however, mostly solids. When used as oxidizers in solid propellants they are superior to NP or AP. Replacement of NO₂-groups by difluoramine might, however, lead to liquid compounds. It seems that this replacement is possible under certain acidic conditions (ref. 33; also preliminary experiments at N.Y.U.) but these conditions have never been really determined.

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The synthesis of N,N,2,2,2-pentanitroethylamine, a compound with the formula $(\text{NO}_2)_3\text{CCH}_2\text{N}(\text{NO}_2)_2$, is attempted by Aerojet starting from nitromethane, formaldehyde and ethyl carbamate (ref. 39). They have proceeded so far to the compound $(\text{NO}_2)_3\text{CCH}_2\text{N}(\text{NO}_2)\text{CO}_2\text{Et}$.

The new entity $\text{-N}=\text{NF}$ is present in the liquid mixed adduct of methylmethacrylate and a N_2F_4 -NO mixture, obtained at room temperature and sub-atmospheric pressure according to the following equation (ref. 36):



The adduct is, of course, no suitable oxidizer; but olefins such as isobutylene and 2-methyl-2-butene reacted similarly with the gaseous mixture giving complex liquid mixtures. (Remark: The adduct of isobutylene and the $\text{NO-N}_2\text{F}_4$ mixture is particularly interesting because of its relation to IBA!).

6. O-N-F compounds.

-ONF_2 compounds can be synthesized by adding N_2F_4 to substrates containing $\text{FC}=\text{O}$ groups or by the " F_3NO " route involving addition of F_3NO to unsaturated bonds.

General Chemical Div. (ref. 30) prepared for instance the compound $\text{FC}=\text{O} - \text{ONF}_2$ via the gaseous reaction of $\text{FC}=\text{O} \cdot \text{O} - \text{O} - \text{CF}=\text{O}$ with excess N_2F_4 . But neither in this nor in other cases was the desirable compound $\text{F}_2\text{C}(\text{ONF}_2)_2$ obtained.

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The BF_3 catalyzed addition of F_3NO to olefins has been described on page 94 of reference (5). Other catalysts are AsF_5 or SbF_5 (ref. 30). But the addition reaction is quite selective: F_3NO acts frequently also as a fluorinating agent.

7. O-F Compounds .

Experiments towards the preparation of OF compounds by reactions of OF_2 with organic and inorganic materials have been discussed before (p. 26). In spite of the beautiful chemical work no new developments with organic OF-compounds can be reported at this time which might be of interest for liquid propellants. Also all attempts have failed to prepare OF-compounds where the OF group is attached to nitrogen (ref. 29).

8. Mixed Oxidizers .

Mixtures of oxidizers are being investigated by many organizations. The reasons for the great interest in such mixtures are numerous. Improvement in physical-chemical and handling properties, reduction of sensitivity, increase in specific impulse or density impulse are just a few examples of the advantages sought by mixing two or more oxidizers.

The choice of the constituents of the mixture depends, of course, on the specific improvement required - there is no panacea which will cure every trouble at the same time.

The situation is well illustrated by a few figures presented by Reaction Motors at the Tampa meeting, (ref. 40). The mixed hydrazine type fuel MHF-3 (14% N_2H_4 , 86% MMH) gives with ClF_3 as the oxidizer a theoretical Isp

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of 285 sec. and a theoretical density impulse of 410. Adding 25% of ClO_3F (PF) to CTF raises the I_{sp} to 292 sec., but the density impulse does not change. For an increase in density impulse the very dense oxidizer BrF_5 must be added; this reduces, however, again the specific impulse.

The increase in I_{sp} by adding ClO_3F is obviously due to the presence of oxygen, which takes care of the carbon in MHF-3. For the same reason "the performance of the two component oxidizer (ClF_3 - ClO_3F) is with most MHF compositions superior to that of the individual compounds". ClO_3F is also used in Triflox, an oxidizer mixture proposed by United Technology Corporation (ref. 41, p. 30); here again it takes care of the carbon contained in the binder of the hybrid engine grain. A 25% improvement in the payload capacity of certain typical ballistic missiles is claimed in comparison to using the neat oxidizer.

Mixing various constituents has also been suggested by many organizations as a means to reduce the sensitivity of certain high energy oxidizers. The sensitivity of compounds, such as compound "R" or compound "A", can be supposedly reduced by an order of magnitude by admixing equal amounts of N_2F_4 . Accordingly a 50/50 mixture of compound "R" and N_2F_4 was used by Minnesota Mining and Manufacturing Co. in a mixed oxidizer, called Moxy-2a, which contains 46.5% b.w. of compound "R", 46.5% b.w. of N_2F_4 and 7% b.w. of ClO_3F . Based on laboratory experiments it was stated that Moxy 2a meets all requirements and is completely safe; (ref. 5, p. 39). But when the Air Force carried out engine tests with Moxy-2a they blew up a few engines; (ref. 29). Aerojet is now trying to find out the reason for the mishaps. Formation of explosive intermediates or an adverse change in the vapor phase composition with temperature have been suggested as the causes for the failure. Clearly the explosions have to be

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blamed on something which did not show up in the laboratory tests, the results of which nobody will doubt. It must be something connected with the firing of the engine, in all probability something comparable to the reason for the trouble which Aerojet experienced some years ago with the jet fuel-nitric acid system. Both the jet fuel and the nitric acid were also innocent propellants. One might expect therefore with interest the results to be obtained by Aerojet in their small scale laboratory combustor with the Moxy-2a-N₂H₄ system. But, Aerojet and many other people will also remember that the trouble with the jet fuel-nitric acid system could be resolved only for engines up to a thrust of 5000 lbs.

Moxy-2a is not the only mixed oxidizer which turned out in practice to be much more dangerous than expected. Also Triflox (70% b.w. N₂F₄, 20% b.w. ClO₃F, 10% b.w. ClF₃) gave bad explosions when the oxidizer was mixed at United Technology Center for motor firings (ref. 42).

But the general opinion seems to be that all difficulties can be overcome, at least with some of the proposed oxidizer mixtures. In fact the Aerojet Corporation has been directed by the Army to work with mixtures rather than with neat oxidizers in their evaluation of high-energy materials for liquid propellants (ref. 43). They list quite a number of binary oxidizer mixtures such as N₂F₄/CTF, ClO₃F/CTF, N₂F₄/R, A/N₂F₄ and also Moxy-2a which will be studied for stability and shock propagation using all the conventional laboratory tests. But tests in the small scale combustor are probably among the most important ones, although they have also their limitations. Incompatibility, separation of liquid phases and reduced storability are serious problems with some of the mixed oxidizer systems. Compound "A" appears to behave exceedingly well with respect to these problems. Rocketdyne reports that the following systems are

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compatible and miscible at low temperatures: $\text{NF}_3\text{O}/\text{A}$; $\text{N}_2\text{F}_4/\text{A}$; $\text{ClO}_3\text{F}/\text{A}$; TNM/A . It is remarkable that TNM and compound "A" are compatible because TNM and ClF_3 are not. However, when the system TNM/A was kept for 24 hours in stainless steel containers at a temperature of 71°C . some reaction and decomposition occurred (ref. 8). All the oxidizer mixtures listed so far are either packageable or space storable or at least intended to be applicable as such.

Cryogenic mixtures of fluorine and oxygen called FLOX have been recently proposed in order to boost the performance of liquid oxygen (ref. 8). General Dynamics Corp. has a contract to replace in the Atlas missile LOX by a mixture of 30-40% fluorine with 70-60% oxygen. Supposedly no major engineering changes are required. (It is also planned to replace the fuel RP-1 by the tetramer of isobutylene which is a much better coolant than the present fuel.) FLOX is superior to F_2O as a substitute for LOX, one of the main advantages of FLOX being that the ratio of fluorine to oxygen can be varied over a wide range to tailor it to the requirements of the fuel used (i.e. oxygen to take care of the carbon and fluorine of the major part of the hydrogen). Rocketdyne is interested in using FLOX in combination with RP-1 as the fuel.

Boosting the performance of the Atlas missile by using FLOX as the oxidizer is in a way a more modest alternative to strapping solid propellant booster rockets to the Titan 2.

Both changes are intended for space applications. Therefore, not only the Air Force but specifically also NASA is very much interested in the development of FLOX.

The Air Reduction Co. is still promoting liquid oxidizers consisting of mixtures of ozone and fluorine.

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Solutions of various salts (e.g. hydrazinium diperchlorate) in hydrazine have also been proposed as oxidizers. Nitroniumperchlorate can, of course, not be dissolved in hydrazine or any amine type fuel. But it might be possible to suspend enough of it in a gelled fuel of this type for use as an oxidizer, provided it can be protected by applying a coating to nitronium perchlorate. A few words on the present status of application of coatings to NP, may therefore, be pertinent. Union Carbide (ref. 44) has developed a coating, called RETA; in this process a primary layer of some organic material, probably dichlorostyrene is polymerized in situ on NP particles after deposition in high vacuum, and a secondary layer of poly-monochlorostyrene is deposited on top of the primary layer. RETA coating is not equally resistant to all materials. However, Thiokol Chemical Co., Elkton Div., reports (ref. 45) that RETA coating behaved quite well in moist air (dynamic tests) and in Dow 550, a reactive phenyl silicon oil. They were less satisfied with the AP coating on NP which has been developed by National Research Corporation (ref. 46), in spite of the fact that the AP coating is protected by a second layer of aluminum. National Res. Corp. thinks that a top-coating of RETA might significantly improve the protection provided by their process. Attempts of Callery Chemical Co. to replace the AP coating by a coating of quaternary ammonium perchlorates gave not more than a "significant improvement in the resistance of NP".

At the present state of the art RETA coating is the most effective protection for NP. In spite of its shortcomings RETA coated NP might possibly be suitable for certain types of solid propellants. But it will doubtlessly take quite some time until the coating has been improved far enough to permit the use of coated NP in gels of liquids - if this will be ever possible at all.

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D. Gels and Slurries

In previous reviews the preparation of gels and slurries and their application to rocket propulsion has been discussed. The goals of these investigations were firstly increasing the safety in handling and operation of rocket propellants and secondly improving their performance (specific impulse and density impulse or both). Now it is also attempted to modify by gelation certain properties of liquid propellants (ref. 47).

These investigations have yielded a large number of figures and results; unfortunately it is not always easy to correlate these figures and to connect results obtained by different or even the same workers, because the experimental methods are not always comparable, because the instrumentation used in these difficult studies is far from being perfect and because fundamental theories are missing which would explain results from a few basic principles. Extension of exploratory studies to emulsions and colloidal solutions is certainly a desirable addition to the work, but it complicates the situation further.

Any attempt to enumerate in the present review in detail the results of these diversified investigations would be a hopeless undertaking and would only serve to confuse the reader. We will, therefore, limit ourselves to a brief survey of the present status of the field, drawing heavily on references (48) and (49); where desirable examples will illustrate the statements made.

At the present time with very few exceptions only gels formed from hydrazine and its derivatives and from amine type fuels are considered for practical applications. The gellants are of the "particulate" type (e.g.

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carbon black, alumina, pyrogenic silica) or of the swellable type.

Comparatively large amounts of particulate gellants are needed (5-12%); but the amount can be reduced by adding surface-active agents. For example MAF-1 (40.5% UDMH, 50.5% DETA, 9.0% Acetonitrile) required 5% b.w. of Cabo-O-Sil for gelation; adding 0.5% of Empol 1014 (a dimer of a C₃₆ acid) reduced the amount to 3.85%. From a large number of tests Aeroprojects concludes that "the effectiveness of a particulate gellant could be enhanced by a bridging agent with functional groups possessing an affinity for the surface of the gellant particles".

Swellable gellants are lyophylic, macromolecules, usually long chain polymers with substituents acting as sites for cross-linking. Typical swellable gellants are Guar Gum, (4-5% protein, mannose chain, galactose branch), CMC (carboxymethyl cellulose), methyl cellulose, Carbopol and Gantrez (the two last are substituted polymethylenes). Swellable gels give, however, sometimes only thickening of the liquid and also otherwise the gellants have to be cross-linked in order to give satisfactory properties of the gel. Compounds such as aluminum octoate, Al-stearate etc. are used for this purpose. Only 2-3% of swellable agents are usually required to produce satisfactory gels and the resulting products are extremely cohesive and elastic. This and the fact that the gellants are combustible give the swellable gellants frequently an edge over the particulate ones. The following table abstracted from reference (49) lists some typical amine fuels gels.

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Table 13.

Summary of Amine Fuels Gelled

(Figures are weight percent of gellant)

Gellant	MMH	UDMH	MAF-1	MHF-1	MHF-3	MHF-4	N ₂ H ₄	Nature of gellant
<u>Particulate:</u>								
Acetylene Black	6.5	6	5		poor at 7	reacts	reacts	
Cab-O-Sil H 5	6.5	7	5	5	6	6	no gel	silica
<u>Swellable:</u>								
Et-435			i	3	3.5	i	1.7	polyvinyl toluene sulfonate
{ Methocel 8000 Al-Acetate			1.6 0.4					methyl cellulose
{ CMC-7 HOP Al-Acetate		i	i	0.8 0.4	i	1.6 0.4	1.2 0.4	carboxymethyl - cellulose
{ Jaguar A-20-D Al-stearate			i		poor gel		1.0 0.5	Guar Gum
{ Cellosize QP 15000 Al-octoate	1.5 0.75		1.3 0.5		1.5 0.5			hydroxyethyl cellulose

40.5%	23.3%	14.0%	32.5%
UDMH	N ₂ H ₄	N ₂ H ₄	N ₂ H ₄
50.5%	45.3%	86.0%	50.5%
DETA	MMH	MMH	MMH
9.0%	31.4%		17.0%
CH ₃ CN	N ₂ H ₅ NO ₃		N ₂ H ₅ NO ₃

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Besides this type of fuels also other materials, such as RP-1 and oxidizer, such as CTF, BrF_5 , F_2O and H_2O_2 have been gelled. With oxidizers clearly only inorganic particulate gellants can be used; even carbon black has to be added with extreme care. Chlorinetrifluoride gelled with this material has exploded on handling. All gels have, of course, to be stable and cohesive, resist temperature cycling, vibrations and accelerating forces. They should in general, become liquid under a certain stress (at the "yield point") which is for rocket applications somewhere between 300 and 1200 dynes/cm², on removal of the stress the liquid should as a rule turn again into a gel within a shorter or longer period of time (thixotropicity). The yield point is not an absolute constant, but has been observed in certain cases (MHF-3 gelled with cellulose acetate) to rise within 12 days by a factor of nearly ten; (ref. 50). But in certain cases also "pseudoplastic gels" (with apparent viscosity varying progressively with stress) are acceptable and even paste-like materials can be injected into rocket engines and burnt successfully. But thixotropicity is very desirable; it is essentially for one of the primary purposes of developing gelled propellants, namely increasing safety of handling. It is essential for the use of self-scaling tanks in space (ref. 43). One requirement must, however, be always fulfilled: the material whether a true thixotropic or a pseudoplastic gel must be stable; no separation of the constituents under various conditions is permissible. This indispensable requirement is not always easy to fulfill. Liquids of high polarity present in this and other respects much more difficulty than non-polar liquids; they can usually be gelled only with swellable gellants. For instance a gel of hydrazine prepared with 5-6% of Carbopol breaks down at 165°F. and peptizes in contact with the carbondioxide contained in the air (resp. CO_3^{m}) or with other cations. One hundred of a percent of $(\text{NH}_4)_2\text{CO}_3$ suffices to prevent the procedure for gelling N_2H_4 to work. Blanketing the

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hydrazine during all operations and during storage is an obvious remedy. Also temperature sensitivity is not critical for missiles stored in silos; still a better gellant for hydrazine is urgently needed in view of the planned use of a slurry of aluminum in hydrazine in the Titan 2A (ref. 51). The Titan 2A is just one example of the second purpose of preparing gels, namely increasing at the time specific impulse and density impulse by suspending metals or their hydrides in gelled propellants.

But even for the better known slurry-type propellants performance data are very scarce. The following table taken from a report by NOTS compares the performance of clean hydrazine with hydrazine containing various additives (ref. 50).

Table 14.

Performance of the N_2O_4 - N_2H_4 System with
Metallic Additives in N_2H_4

Additive	Wt. % in fuel		O/F		Pc		Isp 1000-14.7		ϵ Isp	
	theor.	exp.	theor.	exp.	theor.	exp.	theor.	exp.	theor.	exp.
none	-	-	1.4	1.4	1000	1069	293	290	357	350
Aluminum	20	20	1.0	0.41	1000	963	298	283	380	348
Magnesium	30	30	0.8	1.1	1000	1073	296	276	375	357
MgH ₂	20	20	1.2	1.02	1000	1076	299	287	351	331
NaBH ₄	20	20	1.6	0.74	1000	1069	293	290	357	350

The theoretical and experimental performance cannot be compared exactly because the mixture ratios were not identical except in the case of clean

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hydrazine. But the theoretical figures refer obviously to the optimum I_{sp} .

Also suspensions of the materials in the N_2H_4 were used rather than slurries in the gelled fuel. But just the same the figures indicate that the specific impulse was not increased by the additives, whereas the density impulse rose slightly.

Reaction Motors reported some time ago an I_{sp} efficiency of 95% for the system ClF₃/MHF-3 where the fuel was a pseudoplastic gel prepared with hydroxyethyl cellulose.

Alumizine containing about 40% of aluminum in hydrazine gelled with Carbopol is of particular interest at the present time.

The Aerojet General Corp. is cooperating with the Martin Co. in the conversion of the Titan 2 from the N_2H_4 /UDMH mixture to alumizine; but engineering progress is not as fast as desirable because much fundamental and development work has to be done simultaneously.

Besides Aerojet and Martin-Narietta also practically all organizations in the rocket industry are contributing to the investigation of gels and slurries. It is anticipated that as a result of this work and with the development of special components and measuring devices the overall performances of metallized gelled fuels will reach at least the efficiency of 92% which is required in the case of alumizine to make its use worthwhile. But it probably will require quite some work to reach this figure with an aluminum loading around 40% by weight. The slurries to be prepared or studied include mainly suspensions of Al, AlH_3 , Be, BeH_2 in the fuels discussed above, in some cases also in RP-1.

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Real and substantial improvement in specific impulse can be expected only from the use of Be, AlH_3 or BeH_2 as additives. (Compare e.g. Table III, Ref. 2). But both the Navy and the Army can, because of their toxicity not use Be or BeH_2 ; on the other hand the Air Force is very much interested in their application.

Attempts to prepare slurries of Be or BeH_2 in cryogenics propellants (Aeroproject, Atlantic Research Corp.) are still in the infancy, so are studies of tripropellant systems containing besides usually cryogenic fuels and oxidizers also metals or their hydrides in some carrier (UTC, Aerojet, ARC). Discussion of these studies can be safely postponed for one of the following reviews.

The Marquardt Co. has obtained in ramjets combustion efficiencies up to 95% with hydrocarbon slurries loaded with 73% boron. Such slurries have, of course, a very high volumetric combustion value which is decisive in air breathing engines. But injection in the combustion chamber of rockets requires complete redesign of the injector. No results of tests with rocket engines were reported by the Marquardt Co. at the Tampa meeting.

Mr. Charles J. Thelen listed the goals for the study of slurried rocket-propellants in the immediate future; (ref. 48). In a condensed form they are:

- 1.) Uniform methods for the preparation and evaluation of gels and slurries;
- 2.) Correlation of slurry properties to their stability under mechanical vibration and acceleration forces;
- 3.) Study of combustion properties and performance of slurries in rockets;

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- 4.) Specification of rheological properties of gels and slurries for acceptance in practical flight weight engine designs.

The proposed study of gels for rocket propellants will certainly contribute to the preparation of gels having improved physical chemical properties, the third area of research now under way in this field.

But the Advanced Research Propellant Agency is also sponsoring work having this improvement as the primary goal (ref. 47). The following goals are listed:

- 1.) Stabilize physically incompatible propellants
- 2.) Reduce viscosity at low temperatures
- 3.) Reduce shock sensitivity
- 4.) Increase storability
- 5.) Improve cooling capacity
- 6.) Utilize propellants as gellants
- 7.) Develop special gel characteristics
- 8.) Devise gellants for oxidizer.

There are possibly also other properties, such as thermal conductivity and evaporation rate which might be altered by gelation.

The work has not been going on for a very long time. But it has been demonstrated already that shock sensitivity is considerably reduced by gelling.

For Cavea B the number of cards required for a positive test in the card gap test was reduced from three to zero.

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In the impact test the rating rose for nitromethane from 138 to 182 kg-cm, for hydrazine from 161 to 185 kg-cm. and for n-propylnitrate from 7 to 60 kg-cm.

Altogether progress in the application of gels and slurries to liquid rocket propulsion is possibly not as fast as optimistic advocates predicted some time ago; on the other hand this area is the only one which in combination with light metal hydrides and special oxidizers such as compound "A" holds for the next few years promise of real substantial advancement in liquid rocket propellants.

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III. Monopropellants

1. Heterogeneous monopropellants .

The slurry of $B_{10}C$ in IRFNA called by its proponent "heterogeneous monopropellant" has been discussed in reference 2. This specific composition is chemically not quite stable and also replacement of IRFNA by N_2O_4 does apparently not solve all the problems (ref. 52). Still the concept of the heterogeneous monopropellant appears to be a sound one.

Reaction Motors is screening a number of advanced heterogeneous propellants some of which are listed in the following table taken from reference 52.

Table 15.

Theoretical Calculations for Advanced Heterogeneous Propellants

<u>System</u>	<u>Isp</u>	<u>ξ Isp</u>
AlH_3/N_2O_4	296	434
AlH_3/ClO_3F	294	425
Li_2AlH_5/H_2O_2	291	390
Li_2AlH_5/N_2O_4	281	380
$B_{10}C/ClO_3F-ClF_3$ (10%) (90%)	274	480
$IPQ^{(1)}/N_2O_4$	282	361

(1) IPQ is i-propenyl-carborane

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A slurry of BeH_2 in H_2O_2 would give a heterogeneous monopropellant with a very high I_{sp} ; it is apparently not considered by RMD because of the toxicity of BeH_2 and also because of the low density impulse.

2. Amine type monopropellant for gas-generators .

The Liquid Rocket Propulsion Laboratory of Picatinny Arsenal has continued the study of using Isobel F 2.6^{*)} as a gas generant. The use of the liquid as a gas generant has been previously discussed. It is an "on the shelf" item for auxiliary power applications. The investigation which involves gelled Isobel F 2.6 (6.5% Cab-O-Sil gellant) encountered difficulty in reproduction of ignition and burning characteristics. These difficulties were caused by deformation of the propellant surface due to non-uniform distribution of heat and pressure generated by the pyrotechnic igniter. This area of investigation is continued. It is planned to properly distribute the igniter material over the propellant surface. The purpose of using a gelled gas generant is the hardware configuration which with liquids is too involved for flight applications; (ref. 54).

3. Otto fuel .

Otto fuel, composition 2, (see ref. 41, p. 49) is presently used to propel the Mark 46, model 1 torpedo. Moreover this monopropellant has also been selected to propel the Ex-10 torpedo.

A new 500 HP piston engine, designed by the Clevite Ordnance Corp., Cleveland, Ohio, is presently tested with this fuel. Preliminary results are very encouraging (ref. 53).

*) Isobel F 2.6 is a fuel rich nitric acid solution of ethyltripropyl ammonium nitrate.

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Otto fuel, composition II, is presently manufactured by the Naval Propellant Plant, Indian Head, Md. They produce in their pilot plant 500 lbs. per batch. The Naval Propellant plant is constructing now a plant for continuous nitration (BEA 221 process) and will be ready very soon for mass production of the propellant.

Thus possibly for the first time a monopropellant is being used in practice as a primary propellant.

In view of the great amount of experience with this propellant and its anticipated reliability it might be considered as a propellant for applications other than underwater propulsions, provided specific impulse is of secondary importance.

All Otto fuels are unregulated materials; compositions 1, 2, 3 and 4 can be shipped like any normal chemical compound, but drums should not hold more than 55 gallons. An ullage of 5% b.v. and a pressure relief valve, calibrated for 30 psia, are required. (See Appendix B for Otto fuel composition 1, 2, 3 and 4).

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IV. Liquid Propellant Systems

Liquid propellant systems have been discussed throughout the present review in connection with the discussion of particular propellants. The purpose in doing this was to show the impact of new chemical propellants on performance and to demonstrate the progress which can be expected from future chemical work in the field of rocket propellants.

This remark applies particularly to space- and earth-storable systems which have been dealt with at some length in the introduction to Section II. of this review (p. 3).

We will, therefore, limit ourselves in the following to discussing systems which have not been mentioned previously.

a) Space storable system

Work on the $F_2O-B_2H_6$ system is continuing. Combustion efficiency is very good only within a narrow range of mixture ratio. Before practical application of this system, the reason for this limitation has to be established. Also certain fundamental properties (heat transfer etc.) have to be determined and cooling methods (ablative cooling) have to be developed, (compare ref. 5).

b) Earth storable systems

1.) Packageable propellant systems using amine-type fuels have been discussed before including the possible improvement from the use of compound "A". It might be emphasized again that the Bullpup (developed by the Navy and Reaction Motors) using an amine type propellant system (MAF-3/

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IRFNA) is operational. The AGENA engine (Air Force and Lockheed) is using the UDMH-IRFNA engine and has proven to be an excellent work-horse; (ref. 8).

2.) The B_5H_9 -IRFNA system. It has been suggested to replace UDMH in the latter system by pentaborane (ref. 8) in order to increase performance, the theoretical I_{sp} of the B_5H_9 /IRFNA system being 298 sec. compared to 272 sec. of the UDMH/IRFNA system. But the respective density impulses are (at maximum I_{sp}) 348 sec. vs 345 sec. and the difference in cost of the two systems is very great. Also the I_{sp} efficiency of the B_5H_9 -system is probably lower than that of the UDMH system (solid or liquid boron oxides in the exhaust!). Therefore, B_5H_9 would be useful only in very special applications.

3.) The B_5H_9 - N_2H_4 system. Further investigation of the B_5H_9 - N_2H_4 system has been definitely abandoned by the Air Force (ref. 8). Both the Air Force "in house" and the Rocketdyne program are discontinued. The reasons for the stoppage of the work are that the desired performance of at least 90% (I_{sp} about 300 sec.) could not be obtained consistently and that combustion was invariably unstable; when in a 30,000 lb. thrust engine an I_{sp} of 300 sec. or better was reached. Addition of about 20% MMH to the N_2H_4 eliminated instability but the penalty in I_{sp} was too high. The cost factor might also have contributed to the decision. To the high price of the propellant the great expense for fabrication of the injectors had to be added, which had for a 30,000 lb. engine up to 5000 very fine holes. Also the injector ports had to be recessed and specifications were exceedingly tight. The large amount of solids in the exhaust did apparently not affect performance too badly probably because the boron nitride formed in the combustion chamber was exhausted as an extremely fine dust. But it was extremely difficult to avoid side reactions because of the complicated kinetics and reaction mechanism.

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On paper the $B_5H_9-N_2H_4$ system had looked very attractive. The theoretical performance is with 330 sec. "the largest of any storable propellant system available at the present time in large quantities"; (ref. 55). Sufficient funds and great amounts of propellant were available for a thorough study of the system. It is, therefore, interesting to find the reason for the failure. In all probability it was the fact that the system is lacking overall simplicity. The reaction mechanism is complicated, the reaction rate is slow, very involved injectors are required and also the operation of the system is rather delicate.

In spite of its apparent excellence the $B_5H_9-N_2H_4$ system could, because of its complexity, not succeed.

c) Cryogenic Systems; the H_2-O_2 propellant combination

In sharp contrast to the $B_5H_9-N_2H_4$ system the liquid hydrogen-liquid oxygen system is very simple in most respects. The reaction mechanism is not too complicated, although it has not been completely elucidated; certainly by far less molecules participate than in the $B_5H_9-N_2H_4$ reaction. The reaction rate is very high. Injector and chamber design can be exceedingly simple as will be discussed presently.

As a result combustion efficiency is very high, the residence time in the combustion chamber (measured not quite correctly by the L^*) can be very short and fabrication can be inexpensive and expeditious. Instability of combustion remains, however, a problem.

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1.) Simplified Design .

The Air Force and Aerojet have designed for the operation of the H_2-O_2 system an injector consisting of a single hydrogen jet surrounded by four oxygen jets (Project Scorpio; see reference 5). Engines up to 50,000 lbs. thrust have been fired with a c^* efficiency of 94% at L^* of 30, 40 and 60 inches. Lower efficiencies were, of course, also observed in the course of their test work; for instance, engines incorporating 4 elements of 50 K each and using 6% film cooling gave a c^* efficiency of 87%. It is planned to fire in February a clustered thrust chamber involving eight thrust engines with 25,000 pounds thrust each at an expansion ratio of 5:1 (ref. 56). It seems that the feasibility of substantially simplified engines operating on the H_2-O_2 system has definitely been demonstrated.

It is claimed that the Scorpio principle can be used also for propellant systems other than the H_2-O_2 system e.g. for the LOX/RP1 and for the storable N_2O_4 /UDMH- N_2H_4 system. The extent to which simplification is possible will depend, of course, on the characteristics of the propellant system. The combustion in the H_2-O_2 system is certainly promoted by its high evaporation rate as might be concluded from recent theories, although evaporation rate is clearly not the only factor affecting combustion efficiency. Because of the reduced evaporation rate one might anticipate that simplification of the engine might with the N_2O_4 /UDMH- N_2H_4 system be much more difficult and be possible to a much lesser degree. The comparative simplicity of reaction mechanism of the H_2-O_2 system reduces, of course, the difficulties in obtaining high performance (the opposite is the case with the B-N system). It will be very interesting to find out how far engines for the LOX/RP1 propellant system can be simplified where the re-

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action mechanism is much more complicated than in the H_2-O_2 system, and both the evaporation rate of the fuel and the reaction rates are much slower.

The Scorpio program was not plagued very much by instability. For instance only low frequency oscillations were observed with the single element injector.

2.) Instability .

The problem of instability in the H_2-O_2 system requires, however, in general still very careful attention.

It has been claimed that instability is in the case of this system mainly caused by injecting the liquid hydrogen at too low a temperature (see Ref. 5, p. 52). But it has apparently not been definitely established that temperature effects per se are responsible for instability in the H_2-O_2 system, (ref. 57). Stable operation is not guaranteed by the presence of gaseous hydrogen. Rocketdyne has observed spontaneous instability also with hydrogen at a temperature of $200^{\circ}R$, but on the other hand an injector designed for $200^{\circ}R$. does certainly not give stable operation at $50-60^{\circ}R$. There is no doubt that different factors are involved and that temperature is only one of them although a very important one. This is proven by the fact that a slight change in injector design (recessing of the injector ports) changed at $60-70^{\circ}R$. an instability operation to a stable operation.

Altogether it appears that the causes underlying the instability of the H_2-O_2 system (and actually of all systems) are quite diverse and rather complicated. They are not yet completely understood in spite of the excellent work done by many people e.g. Luigi Grocco and coworkers at

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Princeton. But on the other hand the problem can be and is being overcome in practice by careful injector and engine design and, when necessary, by the use of baffles, which are built into various of the large H_2-O_2 engines by both Rocketdyne and Aerojet.

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V. Thermochemical Panel Meeting

In a confidential meeting of the JANAF Thermochemical Panel held on November 7th, 1963 (ref. 16) some figures of interest for calculating the performance of new rocket propellants were presented and discussed.

Some of them are reported in the following:

a) Hydrides and their derivatives

Dr. D.D. Wayman, National Bureau of Standards, summarized recent values for heats of formation of various hydrides; some of his figures are given in the following list (figures are in K-cal/g-mole and refer to 298°K.)

<u>Compound</u>	<u>ΔH_f (298°K.)</u>
Triaminoguanidine	+ 57.2
$(CH_3)_4N B_3 H_8$	- 34
$B_{10}H_{12} \cdot 2 NH_3$	- 66.6
$B_{10}H_{12} \cdot 4 N_2H_4$	- 23
$LiBH_4$	- 46.4
AlH_3	- 3.0 ¹⁾
$Al(BH_4)_3$	unknown
$LiAlH_4$	- 26.6
Li_3AlH_6 (LAPH)	- 79.4
BeH_2 (95-96% purity)	- 4.5
$(NO_2)_3Al(ClO_4)_6$	- 149
$(NO_2)_3B(ClO_4)_4$	- 80

- (1) Dow Chemical, Olin Mathieson and National Res. Corporation confirmed the value given by NBS for the AlH_3 produced by Dow Chemical; but for Olan 58 (product of Olin Mathieson) Olin and National Res. found a value of about -4.7 Kcal/mole.

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The rather uncertain thermochemical data for Hybalines have been discussed in the section relating to these fuels, (p. 6 ff of this report). All Hybalines show two Isp peaks as a function of oxidizer to fuel ratio depending on the BO and BN condensibles formed. It remains to be seen whether they will show up in practice.

b) C-N-F compounds

The heats of formation of various C-NF compounds is summarized in the following table using figures reported by Dow, Am. Cyanamid and MMM.

Table 16.

Values for the heat of formation of various C-NF compounds

Compound	Code Name	ΔH_f (Kcal/mole) estimated (Dow)	ΔH_f Kcal/mole experimental	Source
$F_2C(NF_2)_2$	H	- 101.9	- 103.7 - 104.1 - 107.7	Dow MMM Am. Cyan.
$FC(NF_2)_3$	R		- 42.5 - 45.1	MMM Am. Cyan.
$C(NF_2)_4$	Δ	+ 15	+ 12.9	MMM
$FC(NF_2)NF$	PFF	- 30	- 31.8	MMM
$(F_2N)_2CFNFCF(NF_2)_2$	F ₁₁ BG	- 44.5	- 75.5	Dow

Am. Cyanamid obtained the figures in the rotating bomb and Minnesota Mining and Manufacturing determined them from explosions.

From these figures the bond energies of the C-N bond was calculated to be 48.2 or 57.4 Kcal/mole (taking the bond energy of the N-F bond as 71.0 or 66.4 Kcal/mole respectively).

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VI. Conclusion

We would like to conclude this evaluation of liquid propellant research with an encouraging observation on liquid propellants made at the 5th Liquid Propulsion Symposium by Dr. Don Ross, Chief Rocket Propulsion Laboratory, Edwards Air Force Base, Edwards, California.

Dr. Ross claimed at this meeting that large liquid propellant engines are inherently more reliable than large solid rocket engines. He showed learning curves for both types of propulsion devices indicating that after a small number of flight tests the reliability of large solid propellant rocket engines (Minute Man) does not improve any more but stays constant at 88%. The reliability of large liquid propellant rocket engines rises much slower but continuously and is expected to exceed the figure of 88% which supposedly has already been reached by the Atlas engine.

The explanation for this behavior is that the comparatively simple solid propellant engine poses to the operating crew much fewer mechanical problems than the liquid propellant engine. They learn fast, but they can learn only to the point where the complexity of the solid grain enters into the picture, but they can do nothing about the grain. The crew of the liquid propellant engine on the other hand must learn to handle an intricate mechanism. This is a difficult undertaking. They learn slowly. But once they have mastered this task the rather simple and thoroughly tested liquid propellant does, as a rule, not pose too many problems.

The main argument against liquid propellants has always been that their reliability is inferior to the reliability of solid propellants.

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This argument does apparently stand up for large engines only with very significant qualifications. Also liquid propellants exceed the performance of solid propellants. Without entering into the many questions arising from the situation described above it can be stated that for large engines liquid propellant systems will in the long run be in many applications superior to solid propellant engines. This conclusion must be, of course, an incentive for intensified research and development in the field of liquid rocket propellants.

In terminating the present evaluation we would like again to apologize for the fact that it is impossible to cover all the diversified areas and all the many valuable papers which are connected with liquid rocket propellants.

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Appendix A.

Materials of Construction for use with Oxygendifluoride

<u>Usage</u>	<u>Liquid Oxygen Difluoride</u>	<u>Gaseous Oxygen Difluoride</u>
Storage Tanks	Stainless Steel 304L (300 Series); Aluminum 2014, 6061; Monel; Magnesium	Stainless Steel 300 Series; Mild Steel for low pressure; Monel; Aluminum 2014, 6061
Lines and Fittings	Stainless Steel 300 Series; Monel	Stainless Steel; Copper; Anodized Aluminum; Mild Steel for low pressure
Gaskets	Soft Copper; Aluminum 2S	Teflon; Aclar; Kel-F
Regulators: Flow	Standard Metal Orifices; turbine meters	Standard Pyrexglass rotameters with stainless steel or aluminum floats
Pressure		All-welded metal Bourdon type; manometer with fluoro- carbon oils; Matheson 15F-670
Injectors	Stainless Steel 300 Series; Copper Nickel	
Pump Materials	Aluminum 2014, 6061; Monel; K-Monel	Aluminum 2014, 6061; Tin
Valve Bodies	9420 Annin; Stainless Steel (Hoketype); Monel K-500; Monel; Aluminum 2014	Monel K-500; 400; 1214 Brass Superior; 55CF70 Matheson Monel; Jamesburg ball valves model D0125, 303 SS
Valve Packing	Packless valve with metal bellows or diaphragm	Teflon
Valve Bellows	K-Monel; Stainless Steel 300 Series	
Valve Seats	Copper; Monel	
Valve Plugs	Teflon	Teflon tape, Teflon O-rings
Thread Sealants and Anticize Compounds	Flared or compression fittings; brazed; Sil-fos soldered; welded	Permatex No. 2; Teflon tape; welded

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<u>Usage</u>	<u>Liquid Oxygen Difluoride</u>	<u>Gaseous Oxygen Difluoride</u>
Bolts, Nuts, Screws	Stainless Steel 300 Series; Inconel X; Monel; K-Monel	
Bearings	Aluminum 6061; Hard Anodize Copper	
Springs	K-Monel; Inconel X; Stainless Steel 300 Series	

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Appendix B.

Constituents of "Otto Fuel" Compositions I, II, III and IV

<u>Constituent</u>	<u>Composition</u>			
	I	II (% by weight)	III	IV
1,2-dinitroxypropane	76.0	76.0	-	-
1,5-dinitroxy pentane	-	-	89.5	-
2,4-dinitroxy pentane	-	-	-	89.5
2-nitrodiphenylamine	1.5	1.5	1.5	1.5
di-n-butylsebacate	-	22.5	9.0	9.0
tributylin	22.5	-	-	-

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